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EVOLUTION OF HYDROGEN CYANIDE DURING COMBUSTION AND PYROLYSIS

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ABSTRACT: The evolution of HCN was determined when materials containing nitrogen in their structures were subjected to combustion and pyrolysis. Any nitrogen-containing material except nitro compounds was found to give off HCN, when heated over 600° C. At extremely high temperature, the evolution of HCN was proportional to the nitrogen content of materials. HCN was also produced by heating a combination of gaseous NH_3 and organic materials.

The processes of HCN formation are discussed.

INTRODUCTION

RECENTLY, PROBLEMS OF smoke and gases from fires have been of growing concern. There are a number of toxic substances which are possibly present in fire smoke and gases. Hydrogen cyanide is one of them, and is considered to be one of the most toxic. The author has reported that HCN is produced when any synthetic polymers containing nitrogen in their structures are burned in air [1]. The amount of HCN produced depends both on heating temperature and air supply. Synthetic or natural polymers, or low molecular weight materials, anything that contains nitrogen, could also produce HCN when they are subjected to combustion or pyrolysis.

This paper describes more in detail about the amounts of HCN produced during combustion and pyrolysis of synthetic and natural polymers, low molecular weight materials, and combinations of ammonia or ammonium compounds and non-nitrogen-containing organic materials. It also discusses the processes of HCN formation in connection with the evolution of ammonia.

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EXPERIMENTAL

The combustions and pyrolyses were carried out in a quartz tube inserted into a cylindrical electric furnace. The collection of HCN, or NH_3 was made with a series of impingers containing KOH, or H_2SO_4 solutions, as shown in Figure 1. The electric furnace was 55 cm long and 4 cm id., and the quartz tube was of 3.6 cm id.

The temperature in the quartz tube was controlled automatically with a temperature controller connected to a stainless steel-sheathed chromel-alumel thermocouple (3 mm in diameter) inserted in the quartz tube. But the voltage of the furnace was manually regulated to minimize the fluctuation of the heating temperature. The thermocouple was situated a little upstream from the specimen so as not to be affected by the decomposed gases and flames.

One of the 4 systems, A, B, C and D shown in Figure 1 was connected to the quartz tube depending on the experiment. System A was used for the combustion in air, and B for the pyrolysis of solid materials. In both cases, the specimen was placed in an aluminum foil boat, and inserted with a spoon into the quartz tube 2 cm from the outlet of the furnace. The insertion of specimen was repeated so that the concentration of CN^- or NH_4^+ could become high enough for analysis. In most experiments, the total sample weight of 1 gram was used. The pyrolysis was carried out using C and D in addition to B. C was used for liquid materials and D for combination of liquid and NH_3 . Experiments were repeated only when the result looked abnormal compared with others.

The duration of heating was 5 minutes or less except for low temperature heating in air and pyrolysis in N_2 which took 10–30 minutes.

Evolved HCN and NH_3 were absorbed respectively in 2N KOH and N/10 H_2SO_4 solutions of 100 ml in total contained in a series of 5 impingers. Each impinger had a 3 cm high solution. The recovery efficiency was confirmed to be 95%.

Prior to HCN or NH_3 analyses, the solutions were shaken with activated charcoal and filtrated for decolorization, and elimination of interferences such as sulfide. Adsorption of CN^- or NH_4^+ by activated charcoal was negligibly small.

For HCN determination, Liebig-Dénigés' silver nitrate titration method was employed, because it is a simple procedure and not affected with most interference for other methods.

For NH_3 determination, Folin's Nessler method [2, 3] was employed, and colorimetry was conducted at 415 m μ 15 minutes after Nessler's reagent was added.

MATERIALS

Synthetic materials used were of a commercial grade. Their nitrogen content which were determined by Coleman Nitrogen Analyzer, are given in Table. Nitrogen-containing low molecular weight materials were reagents of the first grade or higher of the Japanese Industrial Standards.

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Evolution of Hydrogen Cyanide During Combustion and Pyrolysis

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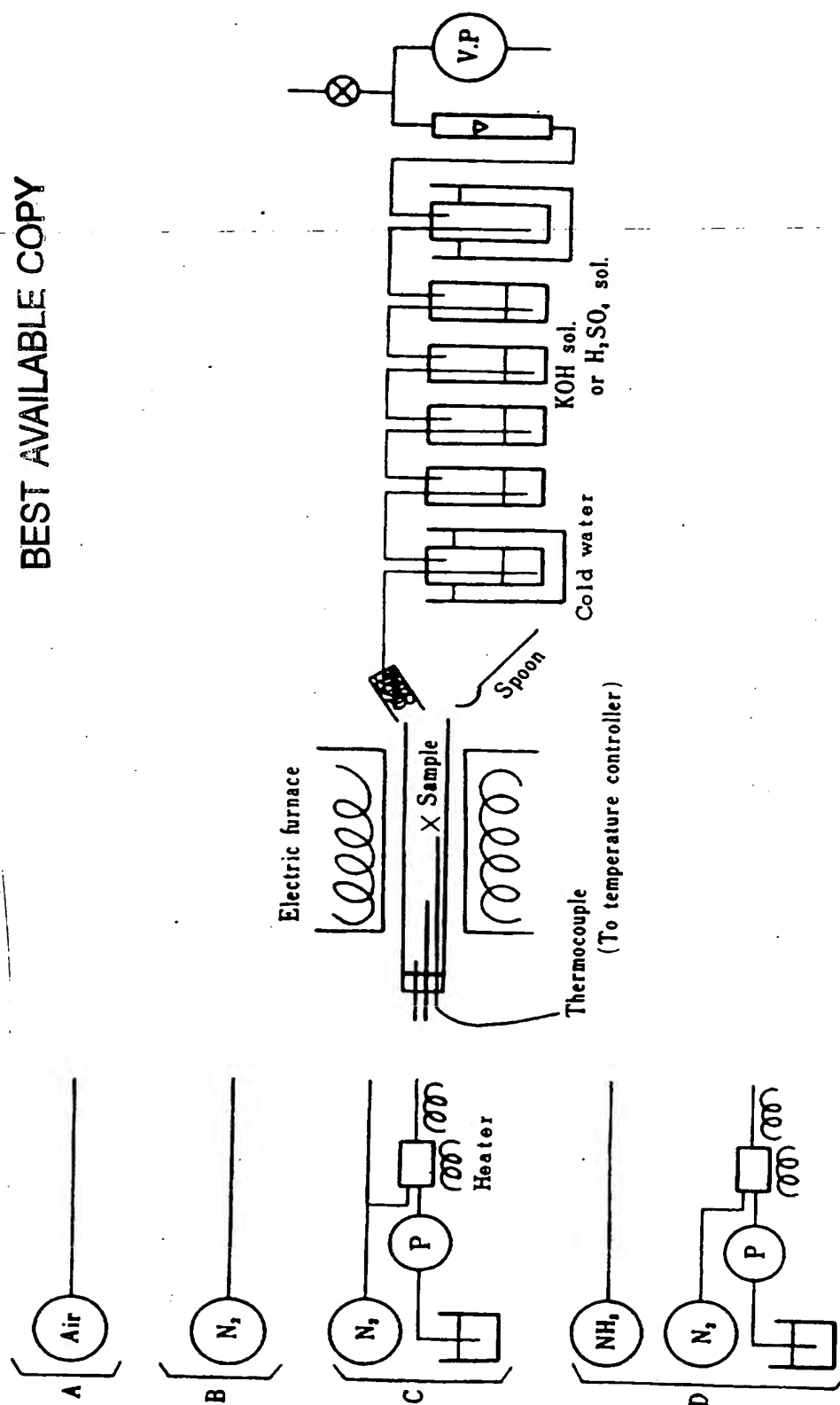


Figure 1. Experimental apparatus

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Table 1. Nitrogen Content of Polymers.

Melamine resin (Pulp content 30%)	32.6 %
Urea resin (Pulp content 25%)	22.7
A.S. Resin	6.64
Polyacrylonitrile	24.0
Polyurethane, flexible foam	6.30
Nylon-6	12.2

RESULTS AND DISCUSSION

Evolution of HCN from Polymeric Materials

The evolutions of HCN during heating of nylon-6 and polyacrylonitrile in air are shown in Figure 2 and Figure 3 respectively. In these figures, the evolutions of HCN at an indicated air supply rate of 0, were actually accomplished in nitrogen gas.

It is described elsewhere [1] that the evolution of HCN is constant when the ratio of air supply rate to sample weight in each insertion is constant. So this ratio can be regarded as a relative air supply rate. The evolution of HCN generally increased with increasing temperature. For most of the heating temperatures, HCN evolution decreased when the relative air supply rate was made too high or too low. That is, there was a maximum in HCN evolution at a certain relative air supply rate. It indicates that oxygen in air, which is involved in decomposition reactions, enhances HCN formation, but consumes the HCN once formed.

The evolutions from urea and melamine resins, and polyurethane flexible foam were little affected by the air supply rate within the range of 0.5×10^{-2} to 2.5×10^{-2} l/min/mg. So, the evolutions of HCN from heating these materials in air were plotted against heating temperature, as shown in Figures 4 through 6. The maximum HCN evolutions from urea and melamine resins were at 650°C, while HCN evolution from polyurethane increased with increasing temperature. Urea and melamine resins did not flame at 650°C or below, therefore, little of HCN produced must have been consumed by oxidation. At 800°C, there was flaming and a sharp drop in HCN evolution. HCN once formed was presumably consumed through flaming combustion by excessive oxygen, because of the small rate of the evolution of flammable decomposition gases. On the other hand, the rate of the evolution of flammable decomposition gases from polyurethane foam was so large that little oxygen was left to consume HCN. So, within the relative air supply rate of 0.5×10^{-2} to 2.5×10^{-2} l/min/mg, the difference in HCN evolution was very small when the same heating temperature was given.

Evolution of Hydrogen Cyanide During Combustion and Pyrolysis

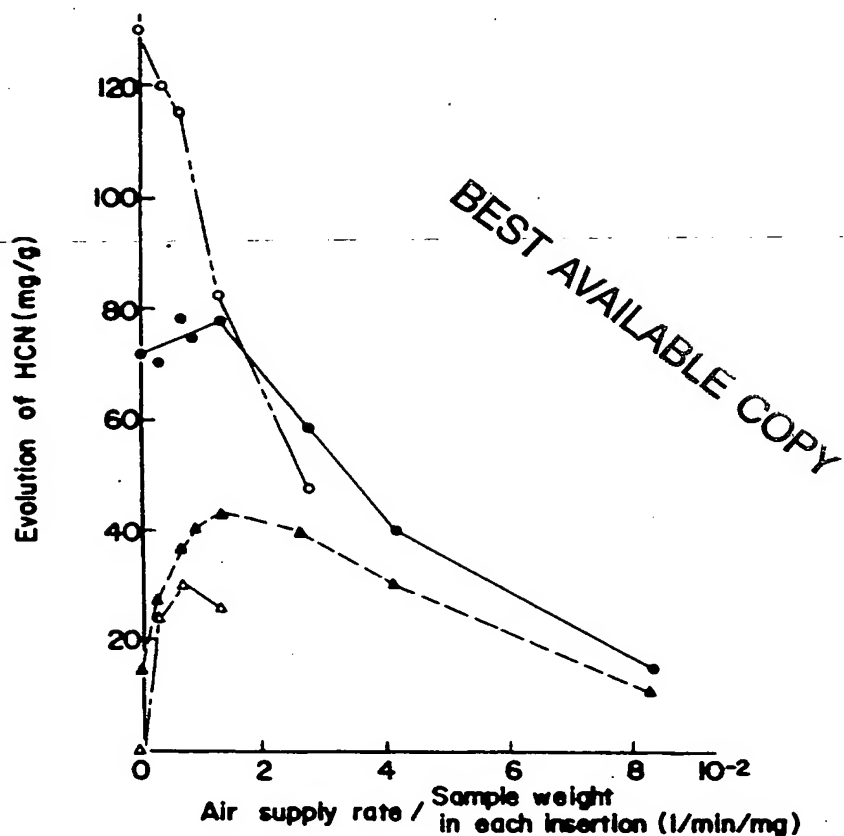


Figure 2. Evolution of HCN from nylon-6 in air.

Heating temperature: \circ 950°C \bullet 800°C \blacktriangle 650°C \triangle 500°C

Sample weight for each insertion: 20–500mg

Air supply rate: 1.83l/min

The evolutions of HCN from various synthetic polymers and from wool heated in nitrogen atmosphere are shown in Figure 7. It seems that HCN evolution starts at about 500°C and increases with increasing temperature. But in the case of polyacrylonitrile, HCN evolution occurred at as low temperature as 300°C. The evolutions of HCN at 900°C shown in Figure 7 were plotted against the nitrogen content, as shown in Figure 8. It was found that HCN evolution is almost proportional to the nitrogen content, and that about 30% of the N in the molecules is converted to N of HCN in nitrogen atmosphere at 900°C. The results indicate that regardless of the atmosphere, air or N₂, HCN formation increases with increasing temperature, because either in air or N₂ decomposition reactions leading to HCN formation become more active at higher temperatures. However, it is possible that in the air, HCN once formed is consumed by oxidation as mentioned above.

The evolution of HCN was generally greater in air than in nitrogen, as long as the air supply rate was kept quite small. Oxidation reaction, in many cases, leads to the flaming combustion whose temperature is higher than the heating temperature, thus

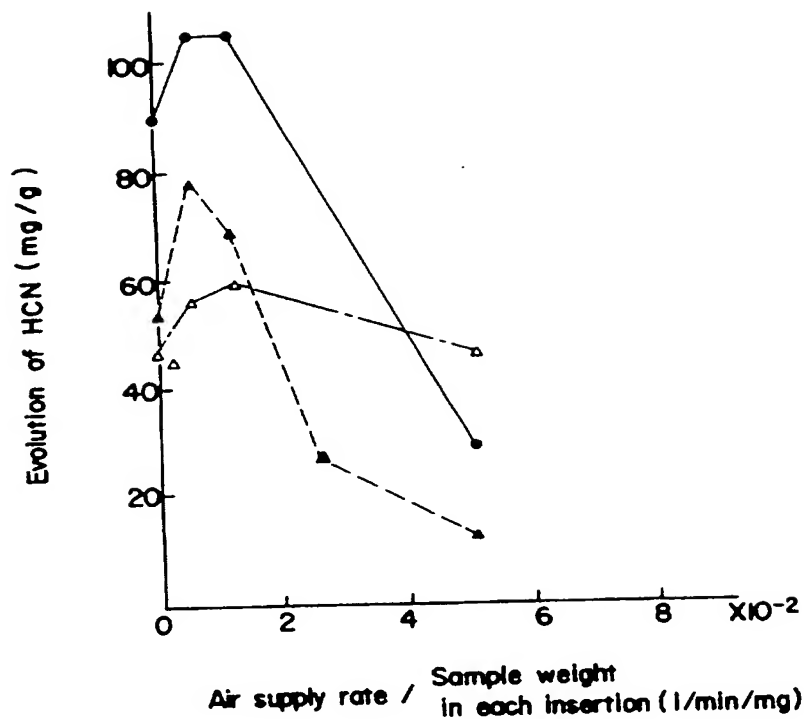


Figure 3. Evolution of HCN from polyacrylonitrile in air.

Heating temperature: ● 800°C ▲ 650°C △ 500°C

Sample weight for each insertion: 140–1000mg

Air supply rate: 1.83–32 l/min

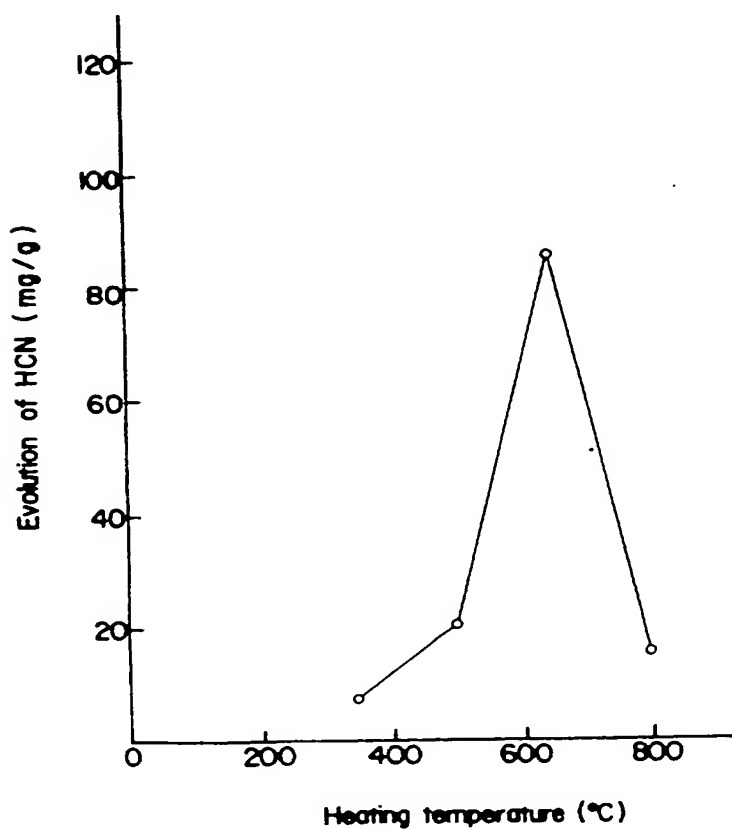


Figure 4. Evolution of HCN from urea resin in air.

Sample weight for each insertion: 140–1000mg

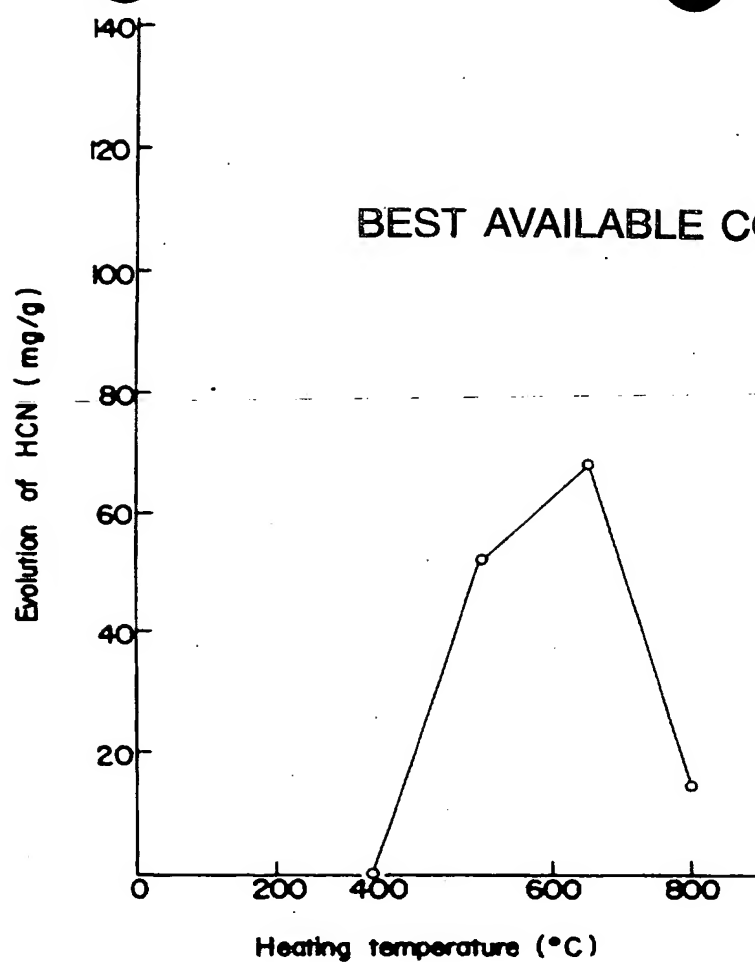


Figure 5. Evolution of HCN from melamine resin in air.
 Sample weight for each insertion: 140–1000mg
 Relative air supply rate: 0.5×10^{-2} – 2.5×10^{-2} l/min/mg

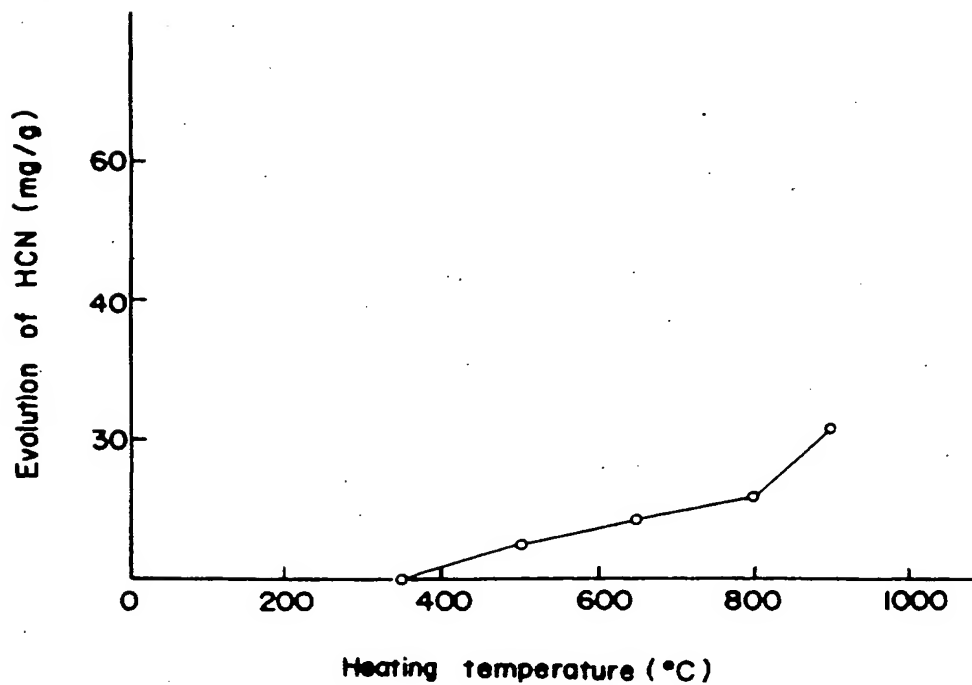


Figure 6. Evolution of HCN from polyurethane, flexible foam, in air.
 Sample weight for each insertion: 140–330mg
 Relative air supply rate: 0.5×10^{-2} – 2.5×10^{-2} l/min/mg

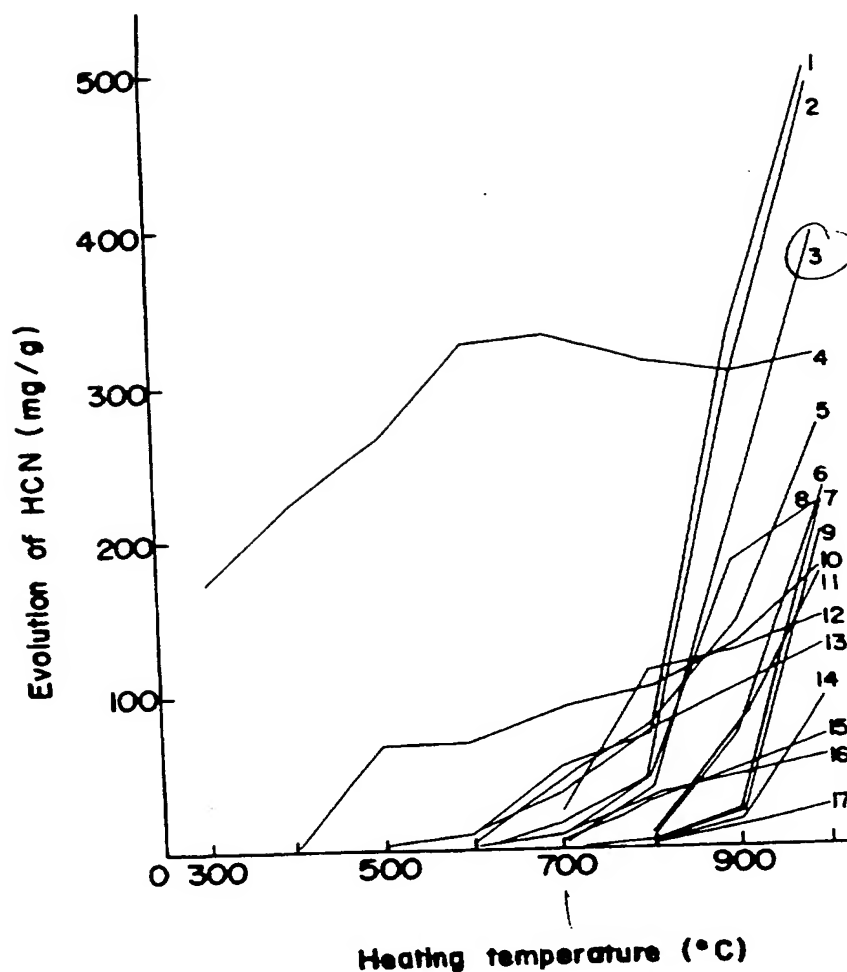


Figure 9. Evolution of HCN from low molecular weight materials in nitrogen gas.

Materials: 1 Melamine, 2 1,3-Dimethylurea, 3 Acrylonitrile, 4 Lactonitrile, 5 N-hexane+NH₃, 6 Pyridine, 7 Phthalonitrile, 8 Ethyl thiocyanate, 9 Acetonitrile, 10 Dimethylglyoxime, 11 Aniline, 12 Hexylamine, 13 Glycine, 14 Acetamide, 15 Urea, 16 Ethanol+NH₃, 17 Azobenzene

acrylonitrile, HCN evolutions from these two are presumed to result from dehydrocyanation.

Although acetonitrile, phthalonitrile, and acrylonitrile have CN radicals, they do not release HCN at low temperatures, probably because their decomposition temperature or the temperature of dehydrocyanation was high.

HCN evolutions at 1000°C in Figure 9 were plotted against the nitrogen content as shown in Figure 10. The plots are considerably dispersed probably because of difference in decomposition temperatures, but, it can still be said that HCN evolution is roughly proportional to the nitrogen content. For some materials, more than

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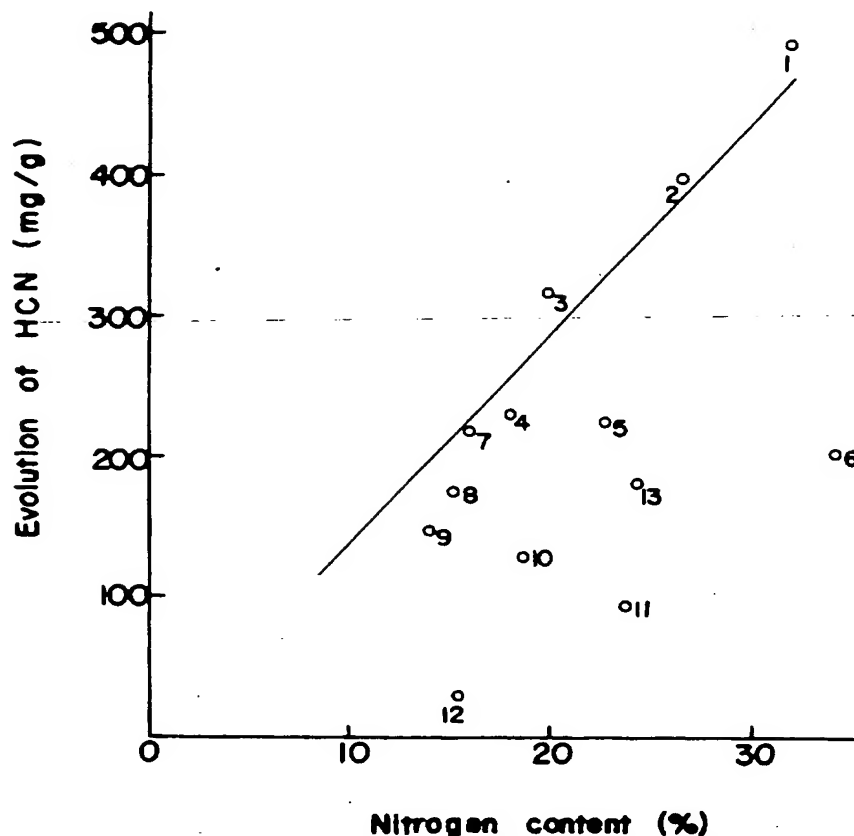


Figure 10. Relation between HCN evolution and nitrogen content of low molecular weight materials

Materials: 1 1,3-Dimethylurea, 2 Acrylonitrile,
3 Lactonitrile, 4 Pyridine, 5 Phthalonitrile,
6 Acetonitrile, 7 Ethyl thiocyanate, 8 Aniline
9 Hexylamine, 10 Glycine, 11 Acetamide,
12 Azobenzene, 13 Dimethylglyoxime

Heating temperature: 1000°C

Atmosphere: nitrogen gas

70% of the N in the molecules was converted to the nitrogen in HCN. It seems that the ratio of HCN evolution to nitrogen content will increase and converge to a certain point at higher temperatures regardless of any difference in the chemical structure.

Evolution of HCN from Non-nitrogen-containing Organic Materials and NH_3

When n-hexane and NH_3 , or ethanol and NH_3 were heated in a nitrogen atmosphere, HCN was produced, as shown in Figure 9. In this figure, the HCN evolution from these mixtures are expressed as HCN evolution (mg)/n-hexane (or ethanol) (g). HCN evolution from these mixtures showed the similar patterns to those from nitrogen-containing compounds. This result indicates that from materials which produce NH_3 in thermal decomposition, HCN can be produced through secondary reactions involving NH_3 .

It can be considered that HCN will be produced from non-nitrogen-containing polymeric materials, if they are involved in high temperature reactions with NH_3 . There is a fear that HCN will be produced when flame retardant fabrics are exposed to fire, if they contain ammonium compounds. In the present study, HCN evolution from cellulosic materials (Toyo filter paper No. 5A) treated with diammonium phosphate was investigated. The HCN evolutions in N_2 and air are shown in Figure 11 and Figure 12 respectively. The tendency of HCN evolution from diammonium phosphate-treated cellulose was found to be almost the same as that from nitrogen-containing materials. The results indicate that when NH_3 or materials which release NH_3 at high temperature are exposed to fire, there is always a possibility of HCN evolution.

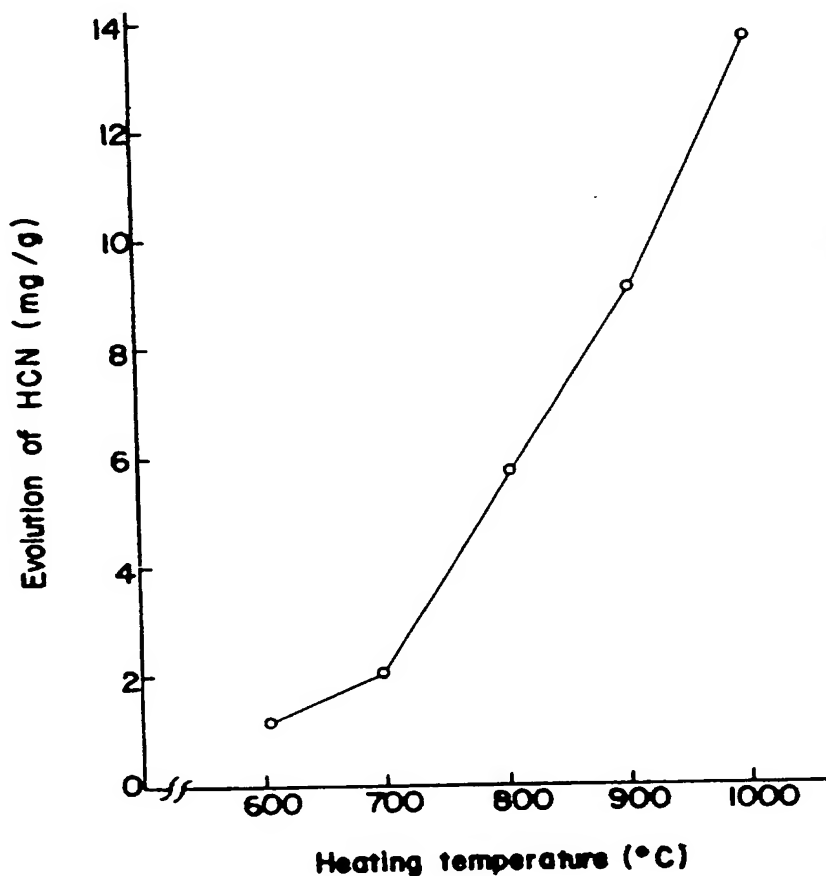


Figure 11. Evolution of HCN from cellulose containing diammonium phosphate of 26.3% in nitrogen gas.

Evolution of NH_3 from Pyrolysis of Nitrogen-containing Materials

The evolution of NH_3 from pyrolyses of polymeric and low molecular weight materials with regard to heating temperatures are shown in Figure 13 and Figure 14

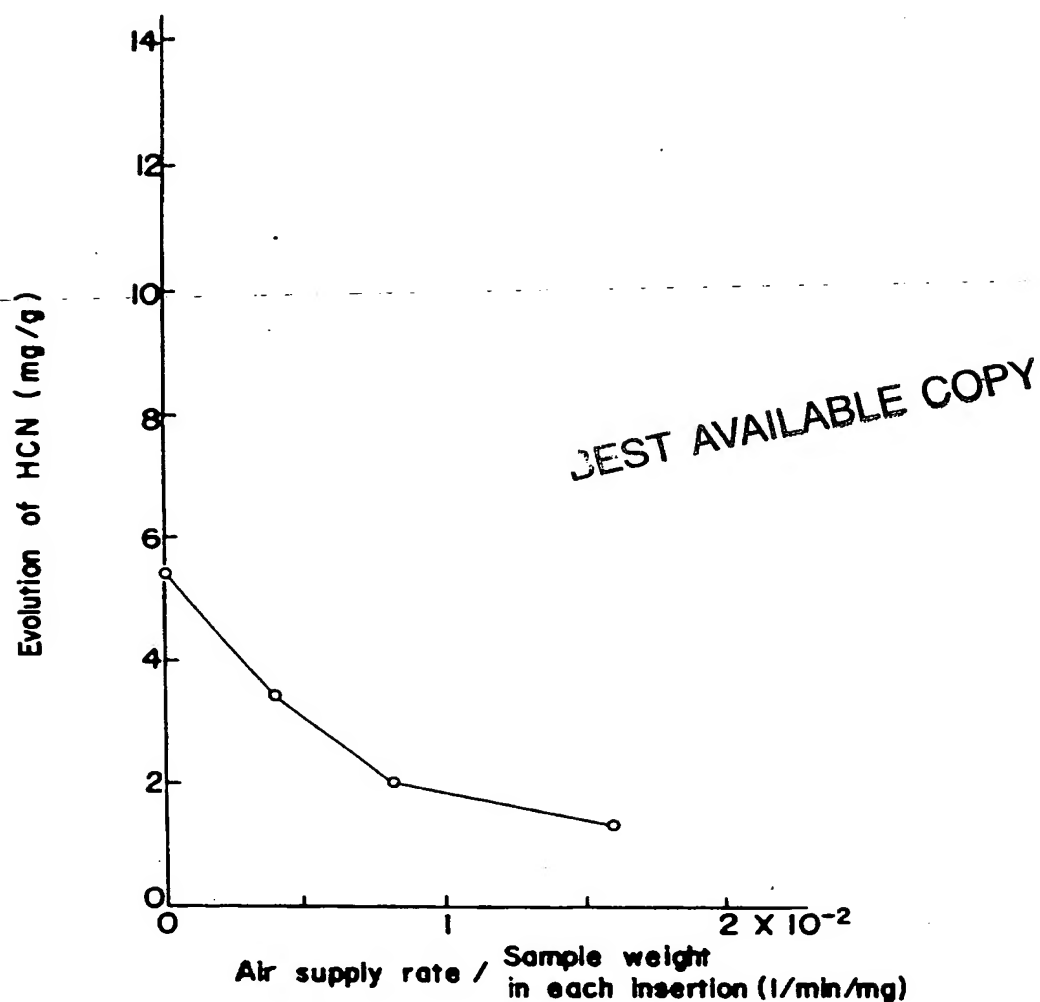


Figure 12. Evolution of HCN from cellulose containing diammonium phosphate of 26.3% in air.

Heating temperature: 800°C

Sample weight for each insertion: 220–440mg

Air supply rate: 1.83–3.66l/min

respectively. The evolution of NH_3 from some materials reached a maximum at certain temperatures, and those from some others decreased with increasing temperature. In such cases, the decrease of NH_3 evolution at high temperatures seems to be at least partly due to the secondary conversion to HCN.

The evolution of NH_3 from some materials increased with increasing temperature. It is feasible to think that when the decomposition reactions become more active at higher temperatures, the increased consumption of NH_3 to produce HCN is masked by the increased evolution of NH_3 at higher temperatures.

It was noted that the NH_3 evolution from nitriles is small without exception. It indicates that HCN production from nitriles occurs predominantly through dehydrocyanation, as has been proposed by others [4, 5].

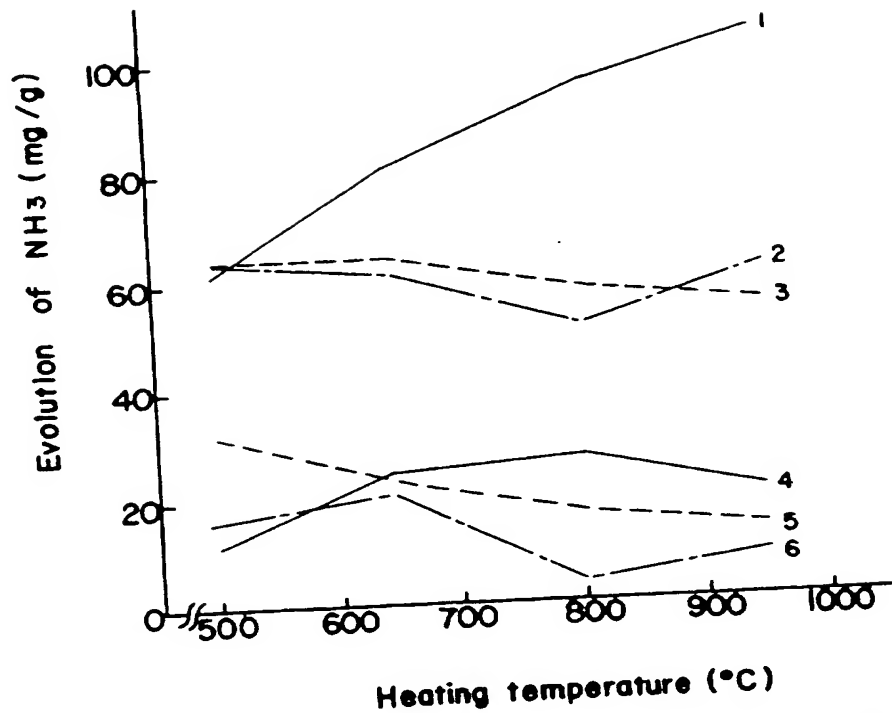


Figure 13. Evolution of NH_3 from various polymers in nitrogen gas.

Materials: 1 Melamine resin, 2 Urea resin, 3 Wool
4 Nylon-6, 5 Polyacrylonitrile,
6 Polyurethane, flexible foam

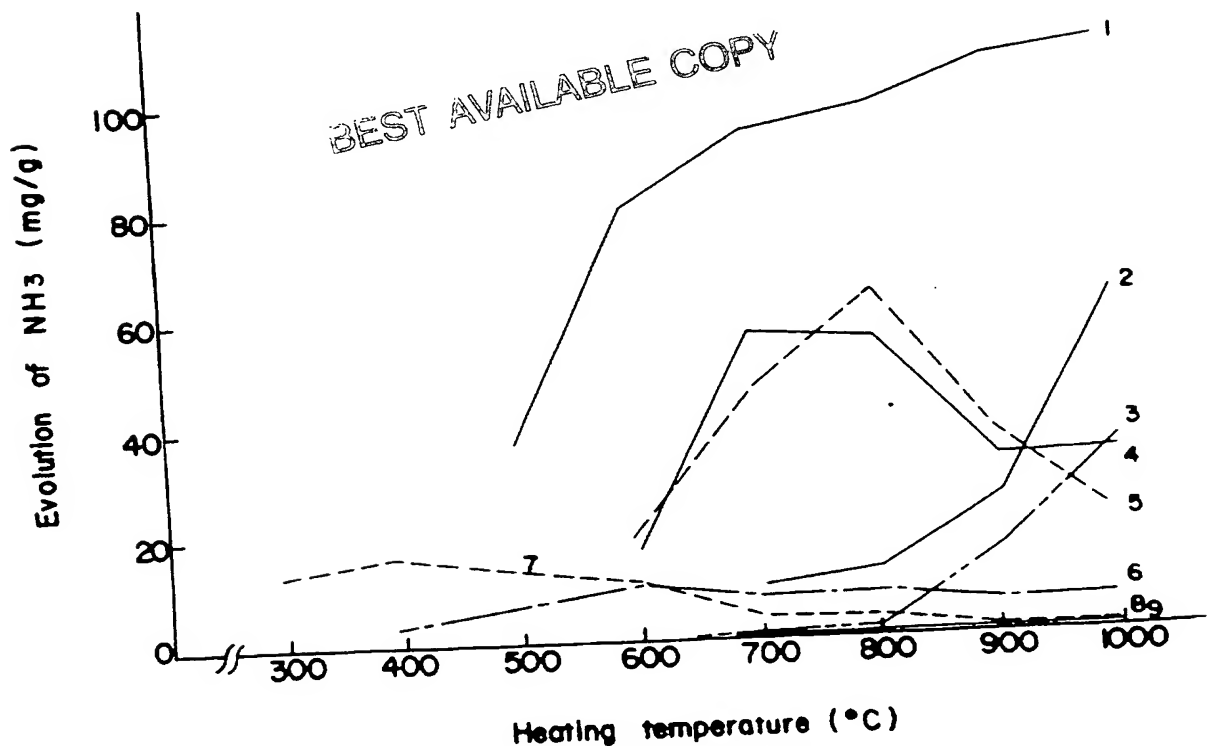


Figure 14. Evolution of NH_3 from low molecular weight materials in nitrogen gas.

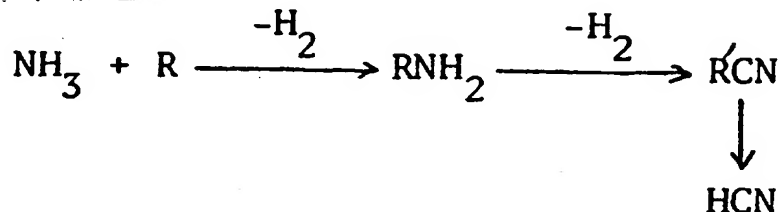
Materials: 1 Melamine, 2 Acetamide, 3 Aniline, 4 Hexylamine,
5 1,3-Dimethylurea, 6 Dimethylglyoxime,
7 Lactonitrile, 8 Acrylonitrile, 9 Acetonitrile

Evolution of Hydrogen Cyanide During Combustion and Pyrolysis

A great part of the HCN produced from other nitrogen-containing materials is supposed to be formed by way of NH_3 .

The process of HCN formation by way of NH_3 may be similar to that of industrial HCN production and include reactions involved in an ammoxidation [1]. So, the following process is proposed.

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But, some HCN is presumed to be produced from original materials or their intermediate decomposition products through dehydrocyanation after intramolecular rearrangements, dehydrogenation, dehydration, etc.

Possible Dangerous Conditions by HCN in Actual Fires

When nitrogen-containing materials, including NH_3 -releasing materials, are involved in fire, the two conditions, i.e., high temperature and low air supply (low oxygen concentration) must be met for great production of HCN. Take nylon-6 for example. If it burns at 950°C under a very low air supply condition, only 1.5 g of it is enough to raise HCN concentration to over 135 ppm (Dangerous concentration for 30 minute exposure) [7] in 1 m^3 space.

In actual fires, at least in the early stage, there is little possibility of the above two conditions being met, that is, a fatal concentration of HCN is not likely to be attained because of a high concentration of oxygen in the early stage of fires. After flashing-over HCN is possibly evolved under the conditions of high temperature and low air supply. In this case, people in other areas of the building could be overcome by HCN flowing out of the fire-filled room.

CONCLUSION AND SUMMARY

Any nitrogen-containing organic materials except nitro compounds, and a combination of NH_3 and organic materials give off HCN when heated over 600°C . Some materials such as polyacrylonitrile, lactonitrile, and dimethyl glyoxime release HCN at such low temperatures as $300\text{--}400^\circ\text{C}$.

Generally, the evolution of HCN is great when the temperature is high and the air supply rate (oxygen concentration) is considerably low.

Under conditions favorable for HCN production, the nitrogen content of materials is proportional to the evolution of HCN.

In actual fires, after flashing-over, there is a possibility that the air flowing from the fire-filled room to the other areas of the building will contain HCN of a high concentration.

There are possibly three processes of HCN formation. One is the direct dehydrocyanation from nitriles, the second a process by way of NH_3 and the last the dehydrocyanation after intramolecular rearrangements, dehydrogenation, dehydration, etc.

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